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# Thermal degradation comparison of amino acid salts, alkanolamines and diamines in CO<sub>2</sub> capture

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## Abstract

In the selection of candidates for post-combustion CO<sub>2</sub> absorption, solvent degradation has become a general concern due to the significant impact on operational cost and the intention to use thermal compression from high temperature stripping to minimize the overall process energy. In this research, structural analogs of amino acid salts, alkanolamines and diamines were thermally degraded in order to explore their thermal stability from a structural standpoint. Functional groups, amine orders and steric effect were investigated for their impact on amine thermal degradation. Primary amines with chain structures showed a thermal stability trend as diamine > alkanolamine > amino acid salt. For alkanolamine and diamine structural isomers, the primary amines are more stable than the secondary amines. Steric hindrance around the amine group was shown to play a positive role in protecting amines against thermal degradation.

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**Keywords:** Thermal degradation; Post-combustion; Functional groups; Steric hindrance

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## 1. Introduction

Among current options for post-combustion CO<sub>2</sub> separation in power plants, aqueous amine absorption is considered the most near-commercial technology. In the development of potential CO<sub>2</sub> absorbents, solvent degradation is a critical concern mainly due to the significant impact on operational cost and the intention to apply

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thermal compression in stripping to minimize the overall process energy. Degradation not only consumes amine, resulting in higher solvent makeup rate, but also induces operational difficulties in the CO<sub>2</sub> absorption/regeneration processes such as raising foaming tendency and contributing to corrosion. It has been reported that the monoethanolamine (MEA) process, the most widely studied absorption technology, has a makeup cost of approximately 10% of CO<sub>2</sub> capture cost [1]. Due to the degradation, the MEA regeneration temperature is limited [2]. Therefore, it is critical to understand the stability of potential CO<sub>2</sub> absorbents to gain a comprehensive evaluation on their potential use as CO<sub>2</sub> absorption agents.

Two main types of amine degradation have been defined in post-combustion CO<sub>2</sub> capture: oxidative and thermal. Oxidative degradation generates oxidized fragments of amines such as organic acids, aldehydes, ammonia and amides. Organic acids could react with amines and give rise to heat-stable salts. Thermal degradation of amines at stripping temperatures generally produces higher molecular weight polyamines, including amine dimer, amine trimer and cyclic amines.

The conventional MEA thermal degradation pathway is carbamate polymerization [3]. In this mechanism, MEA carbamate could cyclize in a dehydrolysis step to form oxazolidone (OZD). Afterwards, another MEA could nucleophilically attack the OZD to reopen the ring and form another major degradation product N-(2-hydroxyethyl)-ethylenediamine (HEEDA). Similar to MEA, HEEDA could react with CO<sub>2</sub> to form HEEDA carbamate, which could in turn form another cyclic product hydroxyethyl-imidazolidone (HEIA). HEEDA can also attack OZD in the same way MEA does to form MEA trimer. MEA trimer can then react with CO<sub>2</sub> to form the cyclic urea of MEA trimer.

Amino acids have been reported to be attractive alternatives to alkanolamines in CO<sub>2</sub> absorption due to their fast CO<sub>2</sub> absorption kinetics and negligible partial pressures [4]. Some amino acid salts have been reported to be more oxidatively stable than MEA [5]. However, the thermal degradation of amino acid salts was only recently studied and was found to have enhanced thermal degradation rates compared to the reference MEA solvent [6].

Several diamines have been attracting growing attention due to their potentially higher CO<sub>2</sub> capacity and absorption rate. It has been reported that ethylenediamine (EDA) generates both monocarbamate and dicarbamate in the reaction with CO<sub>2</sub> [7]. Different concentrations (1.6–4.2 m) of EDA have been tested in the pilot plant for its CO<sub>2</sub> solubility. At an aqueous concentration lower than 2m, EDA was found to have a faster CO<sub>2</sub> absorption rate than MEA [8–11].

In this research, several structural analogs of amino acid salts, alkanolamines and diamines were exposed to high temperature degradation conditions in order to explore their thermal stability from a structural standpoint. The conditions selected were chosen to be relevant to CO<sub>2</sub> capture thermal stripping conditions; CO<sub>2</sub>-loaded solutions were heated to 135 °C and 145 °C under static conditions. Given that CO<sub>2</sub> loading enhances amine thermal degradation [12], this work investigates a severe degradation scenario in CO<sub>2</sub> capture process. MEA was used as a reference. Amine depletion was investigated by ion chromatography (IC), and high performance liquid chromatography-mass spectrometry (HPLC/MS). This research develops a relationship between amine structure and thermal degradation rate. The investigated structural factors include functional groups, amine orders and steric effect.

## 2. Experimental

### 2.1 Thermal degradation evaluation

Thermal degradation experiments were carried out in cylinders constructed of 1/2-inch outer diameter, 6-inch long, 316 stainless steel tubing (10 mL volume) as shown in Figure 1. Detail operations have been previously described in publication [13]. Nitrogen was bubbled through the sample tubes prior to closure to minimize the oxygen in the samples. The sample tube was capped and stored in an oven maintained at a specific desired

temperature. Tubes opened for sampling were not returned for further heating. In order to check leakage, the sample contained tubes were weighed before and after heating. Samples having more than 2.0% solution weight change were considered as leaking samples and therefore excluded from the data set.



Figure 1. Thermal degradation reactor.

IC was performed using a Dionex ICS-3000 system (Dionex-ThermoScientific Sunnyvale, CA). The IC system has an AS 40 autosampler, dual pumps, suppressors and conductivity detectors for simultaneous anion and cation analysis. Cation IC was utilized to identify and quantitate alkanolamines and diamines. An IonPac CG17 guard column (4×50 mm), an IonPac CS17 analytical column (4×250 mm) and a 4-mm CSRS 300 (Cationic Self-Regenerating Suppressor) were used for cation chromatography. The mobile phase was methanesulfonic acid (MSA) in analytical grade water. An isocratic eluent profile was used to separate and quantitate cations. In this program, MSA concentration was set at 18mM for 20min elution.

An Agilent 1260 infinity HPLC coupled with 6224 Time of Flight Mass Spectrometry (TOF-MS) was utilized to identify and quantify amino acid salts. An analytical column Pinnacle DB AQ C18, 50 x 3 mm, 3 $\mu$ m with Restek trident inline filter was utilized. The eluent was 0.10% formic acid in water (A) and in methanol (C). A gradient profile was utilized and described in previous publication [6]. The column temperature was 20 °C. The molecules were ionized by dual electrospray source (ESI) with positive mode of ionization and the mass range was 40-1000 m/z. Complete system control and data acquisition were carried out using the Agilent Mass Hunter workstation software version B.05.00. All samples were prepared with 18.2 M $\Omega$  water for product analysis with HPLC/MS. The extracted ion chromatograms (EIC) were used for product quantification.

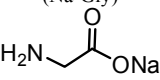
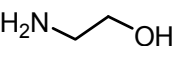
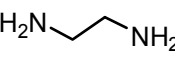
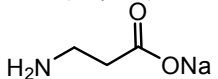
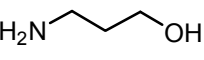
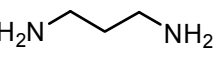
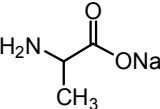
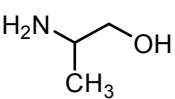
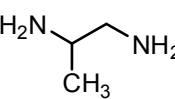
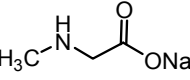
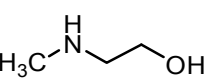
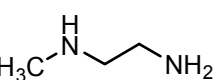
As shown in Table 1, CO<sub>2</sub>-loaded solutions of different structural analogs were thermally degraded at 135 °C and 145 °C for their degradation rate comparison.

### 3. Results and discussion

#### 3.1 Impact of Functional Groups

Comparison of the primary amine analogs with chain structures (first two rows in table 1) demonstrated that change of functional groups impacts amine thermal degradation rates. Figure 2 presents a thermal degradation rate comparison of the sodium glycinate (Na-Gly), MEA and EDA, which are structural analogs with different functional groups, at 135 °C for 100 h. Na-Gly and EDA are the substitution of the hydroxyl group on MEA with a carboxylic acid group and an amine group respectively. These three compounds have similar amine basicity in terms of the amine pK<sub>a</sub> values [6]. The thermal stability has a trend of diamine > alkanolamine > amino acid salt. The same trend was observed in the comparison of sodium beta-alanine (Na- $\beta$ -Ala), 3A1P and 1,3-DAP. The result suggests that, for both two carbon and three carbon backbone analogs, diamines are the most thermally stable species while amino acid salts are the least stable category, reflecting the different degradation mechanism of these three categories. Amino acid salts were reported to mainly undergo amide formation at high temperature stripping conditions, during which the amine groups function as a nucleophile to intermolecularly attack the carbonyl carbon and generate amides [6]. This one step reaction explains the fast thermal degradation rates of amino acid salts. In contrast, the major thermal degradation pathway of alkanolamines was known to be carbamate polymerization [3]. In this process, carbamates initially cyclize to form OZD analogs in a dehydration step. Another alkanolamine molecule can then nucleophilically attack the OZD to re-open the ring and generate alkanolamine oligomers.

Table 1. Amine structural analogs in thermal degradation investigation.

Amino Acid Salts	Alkanolamines	Diamines
Sodium Glycinate (Na-Gly) 	Monoethanolamine (MEA) 	Ethylenediamine (EDA) 
Sodium $\beta$ -Alaninate (Na- $\beta$ -Ala) 	3-Amino-1-Propanol (3A1P) 	1,3-Diaminopropane (1,3-DAP) 
Sodium Alaninate (Na-Ala) 	2-Amino-1-Propanol (2A1P) 	1,2-Diaminopropane (1,2-DAP) 
Sodium Sarcosinate (Na-Sar) 	2-(Methylamino)ethanol (MAE) 	N-methylethylenediamine (MEDA) 

### 3.2 Impact of Amine Order

A comparison of the thermal degradation rate of structural isomers with different amine order, Na- $\beta$ -Ala and Na-Sar, has previously been reported [6]. Na- $\beta$ -Ala, the primary amine, is found to degrade faster than Na-Sar, a secondary amine. Given that the amine groups on these two amino acids have similar basicity [6], the thermal degradation rate difference could stem from the steric effect of the amine group, which could lower the amide formation potential of Na-Sar, and therefore reduce its thermal degradation rate.

Similar to the investigation on amino acid salts, this research compared the thermal degradation rates of several alkanolamine and diamine structural isomers with different amine orders. Figure 3 compares the thermal degradation rate of MAE with that of 3A1P. MAE is a secondary amine, while 3A1P is a primary amine. After 100 h heating at 135 °C, MAE degraded significantly more than 3A1P, suggesting that secondary alkanolamines thermally degraded faster than primary alkanolamines. This result is consistent with a previously reported study where diethanolamine (DEA), a secondary alkanolamine, was reported to be less stable because it is more nucleophilic than primary alkanolamines [14].

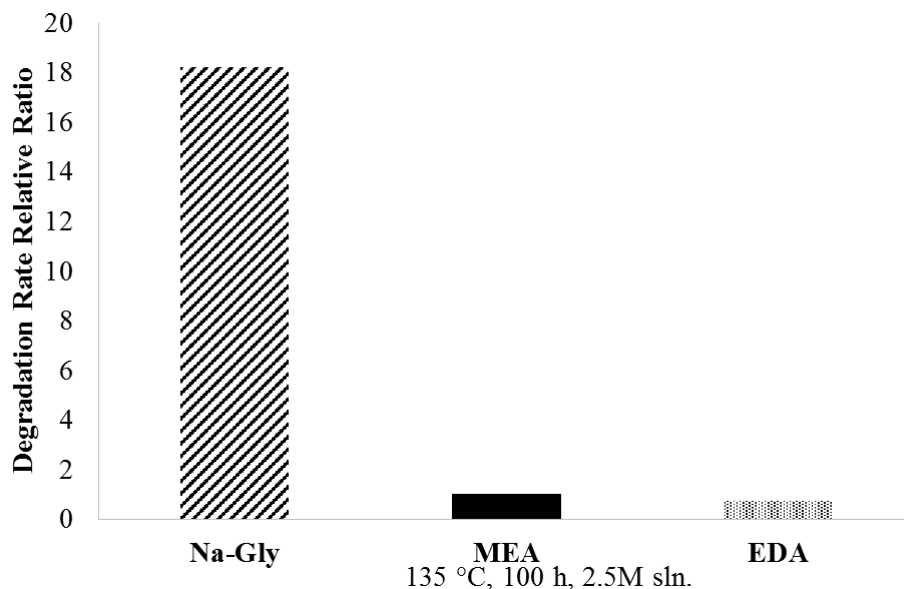


Figure 2. Thermal degradation rate comparison of 2.5 mol/L Na-Gly, 2.5 mol/L EDA at 135 °C with 2.5 mol/L MEA as the reference; Comparison was shown as the relative ratios to MEA loss rate, which was set as 1; Data points were collected for 100 h heating; Amine loss rate was obtained from dividing the parent amine concentration reduction by heating time and normalized to the MEA loss rate.

MEDA and 1,3-DAP are diamine structural isomers with the only difference that MEDA contains one primary and one secondary amine group while 1,3-DAP has two primary amine groups at the ends. Consistent with the observation in alkanolamines, the primary diamine is more stable than the secondary diamine. For both alkanolamines and diamines investigated, secondary amines have higher basicity over primary amines in terms of the different  $pK_a$  values. As a consequence, secondary amines are better nucleophiles and favor higher degradation product formation (like urea generation). Even though secondary amines also have higher steric effect around amine groups, which could slow down the degradation, the higher basicity seems to dominate the amine thermal degradation rate of alkanolamines and diamines.

### 3.3 Steric Effect

In the thermal degradation research of amino acid salts, it could be seen that steric hindrance around the amine group may contribute to the resistance to thermal degradation of amino acid salts [6]. Following this finding, the thermal degradation rates of alkanolamine structural analogs were compared in order to gain a deeper understanding on the role of steric effect in maintaining the thermal stability of alkanolamines. Figure 4 compares the degradation rates of AMP with that of MEA. Compared to MEA, AMP has two additional methyl groups on the  $\alpha$ -carbon to the amine group. Interestingly, the thermal degradation rates for AMP was significantly less than that of MEA, which indicates that higher steric hindrance around amine group does lead to higher thermal stability.

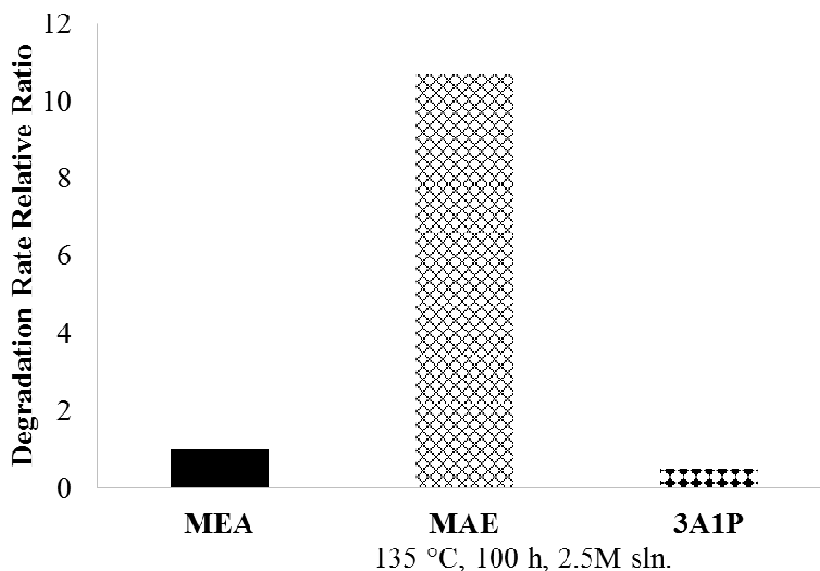


Figure 3. Thermal degradation rate comparison of 2.5 mol/L MAE, 2.5 mol/L 3A1P at 135 °C with 2.5 mol/L MEA as the reference; Comparison was shown as the relative ratios to MEA loss rate, which was set as 1; Data points were collected for 100 h heating; Amine loss rate was obtained from dividing the parent amine concentration reduction by heating time and normalized to the MEA loss rate.

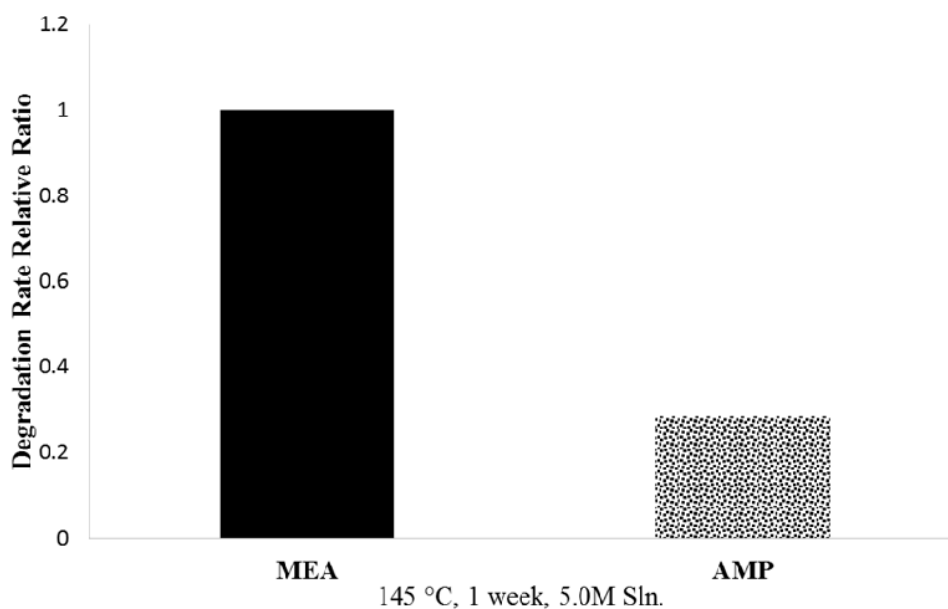


Figure 4. Thermal degradation rate comparison of 5.0 mol/L AMP at 145 °C with 5.0 mol/L MEA as the reference; Comparison was shown as the relative ratios to MEA loss rate, which was set as 1; Data points were collected for 1 week heating; Amine loss rate was obtained from dividing the parent amine concentration reduction by heating time and normalized to the MEA loss rate.

It is believed that higher steric hindrance slows down the carbamate cyclization and thus reduces the tendency to form OZD-like cyclic degradation product. As shown in Figure 5, MEA, without substituted groups on the

backbone, is subject to a relatively smaller electron repulsion in carbamate formation and less strain in OZD ring. In contrast, AMP has two additional methyl groups on the carbon chain backbone, which causes larger electron repulsion in the carbamate. This decreases carbamate stability and could also cause bigger strain in OZD-like compound. In consequence, this reduces AMP carbamate cyclization and explains the higher thermal stability of AMP compared to MEA.

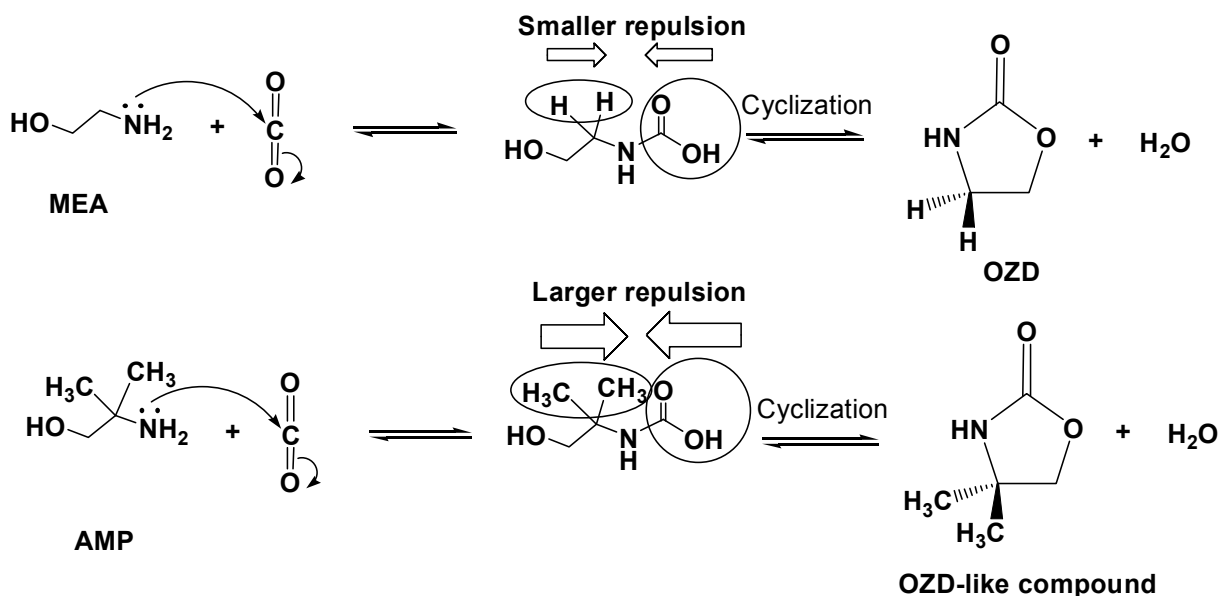


Figure 5. Steric hindrance induces strain in AMP carbamate cyclization with comparison to MEA.

#### 4. Conclusion

In order to establish a structure versus thermal stability model to direct the exploration of CO<sub>2</sub> solvents with high thermal stability, structural analogs of amines were thermally degraded for the degradation rate comparison. Structural factors including functional groups, amine orders and steric hindrance were investigated for their impact on amine thermal degradation. Due to the different thermal degradation mechanism, primary amines with chain structures showed a thermal stability trend as diamine > alkanolamine > amino acid salt. For the investigated amino acid salts, primary amines degrade faster than secondary amines, reflecting the fact that steric hindrance dominates the degradation rates. However, for alkanolamine and diamine structural isomers, the primary amines are greatly more stable than the secondary amines. Secondary alkanolamines/diamines have higher basicity than primary alkanolamines/diamines and thus are better nucleophiles, which favor the degradation product formation (like urea generation). Even though secondary alkanolamines/diamines also have higher steric effect around amine groups, which could slow down the degradation, the higher basicity seems to dominate the thermal degradation of alkanolamines and diamines. As to the studied alkanolamines, the steric hindrance of the amine group is higher for AMP when compared to MEA while the thermal degradation rate was lower, which indicates that higher steric hindrance around the amine group leads to higher thermal stability.

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